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Cancer and Non-Cancer Risk of Santiago Island (Cape Verde) Population due to Potential Toxic Elements Exposure from Soils

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Abstract

The hazard and the carcinogenic risks due to the exposure to some potentially toxic elements by the Santiago Island (Cape Verde) population where calculated, considering soil ingestion, inhalation and dermal contact as exposure pathways. The topsoil of Santiago Island is enriched in Co, Cr, Cu, Ni, V, Zn, Mn and Cd to upper crust values. Hazard indices (HI) were calculated for these metals and As exposures, of Santiago Island population and the calculations were performed for children and adults. For children HI are higher than 1 for Co, Cr and Mn. So there is indication of potential non-carcinogenic risk for children, due to the high Co (HI=2.995), Cr (HI=1.329) and Mn (HI=1.126) values in soils. For the other elements, and for adults, there is no potential non-carcinogenic risk. Cancer risk was calculated for As, Cd, Cr and Ni exposures, for adults and children, and the results are mainly lower than the carcinogenic target risk of $1x10^{-6}$, for As, Cd, and Ni. However, cancer risk is higher than the carcinogenic target risk for Cr, for adults. Regarding As, for children the fraction due to $Risk_{ingestion}$ represents 51.6%, while $Risk_{inhalation}$ represents 48.0% and $Risk_{dermalcontact}$ represents only 0.4% of total risk. For adults $Risk_{inhalation}$ represents 81.3%, $Risk_{ingestion}$ represents 16.6% and $Risk_{dermal\ contact}$ represents 2.1%. These results reflect the higher daily ingestion dose for children and the higher inhalation rate and higher dermal contact surface for adults. For the other elements and for adults the cancer risk due to Cr, Ni and Cd inhalation is always higher than for children, reflecting the higher inhalation rate for adults.

Keywords: cancer risk, risk assessment, volcanic soils, Santiago Island

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1. Introduction

Soils are natural resources, formed at the Earth surface by weathering of underlying rocks by the action of physical, chemical and biologic factors. They are the support of agriculture, the main carbon reservoir of the terrestrial carbon cycle, act as sink for pollutants, protecting groundwater from pollution and are also used as construction material and support. So they have very important social, environmental and economic functions (Vrščaj et al., 2008; Cabral Pinto et al., 2017a).

However, if contaminated or polluted they can transfer potentially toxic elements (PTE) to groundwater, seepage waters and rivers and also to crops and vegetables which are used by humans and animals, and consequently affect human health. The soil contamination may be natural due to rock composition. Some elements can accumulate on topsoil, to concentrations that are toxic to the plant, to the animal feeding on it and to humans. Air quality may also be affect by contaminated soils, by the generation of airborne particles and dust (Gray et al., 2003). In deeper soils due to changes in pH and Eh, the PTE may be released to groundwater resulting in its contamination (Camobreco et al., 1996; Pinto et al., 2004; Mirlean et al., 2007; Neiva et al., 2014).

The chemical composition of dust, soils and groundwater may cause metabolic changes which may favor the occurrence of endemic diseases in humans (Salgueiro et al., 2010; Cabral Pinto et al., 2014; Candeias et al., 2014; Patinha et al., 2015; Reis et al., 2015; Reis et al., 2016; Wu et al., 2015; Centeno et al., 2016; Cabral Pinto et al. 2017b). The role of F, I, Se and As concentrations in the health of human populations is well documented in the scientific literature (Shamberger, 1983; Rayman, 2000; Kinniburgh and Smedley, 2001; Centeno et al., 2002; Tchounwo et al., 2003; Charlet and Polya, 2006; Dissanayake and Chandrajith, 2009; Tisserand et al., 2014; Centeno et al., 2016).

The high concentrations of PTE on topsoil can threaten human health via (a) soil ingestion by geophagism, rare in adults, but quite common in children by hand-to-mouth intake; (b) by inhalation of dust particles and (c) by dermal contact (Sun et al., 2010; Xie et al., 2011), specially by farmers and construction workers and (d) indirectly also by ingestion of contaminated groundwater.

Geochemistry of major, trace and rare earth elements (REEs) of soils of Santiago Island (Cape Verde) has been done in order to characterize soils developed on volcanic

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rocks and Quaternary sediments, contributing to the establishment of a geochemical atlas of the island (Marques et al., 2012; Cabral Pinto et al., 2012; 2014; 2015).

Cabral Pinto et al. (2015) presented the Mapping of Estimated Background Values (EBV), the agricultural and residential Environmental Risk Index (ERI) for each element and the agricultural and residential Multi-Element (ME-ERI), which are the average of the ERIs taken over all elements, for some harmful elements in soils of Santiago Island (Cape Verde Archipelago). The present work follows the precedent study in order to better understand the relationships between environmental geochemistry and public health in a volcanic island which still preserve many pristine geochemical characteristics, where the anthropogenic action is not yet too strong. We present the hazard risk and the carcinogenic risk due to the exposure to some potentially toxic elements by the Santiago Island population, according to the Exposure Factors Handbook (USEPA, 2011). We consider soil ingestion, inhalation and dermal contact as exposure pathways, because most of the population of the Island is rural and the island is affected by strong winds (defined as "bruma seca") which mobilize significant amounts of dust particles from soil (Almeida-Silva et al., 2013).

2. Geographic, geologic and climate settings and soil types

Cape Verde is formed by 10 islands, located at the African western shore (Figure 1). The country capital is located in Santiago Island, which is the biggest island. It is a mountainous island with a maximum altitude of 1394 m. It has 215 km^2 of arable area and estimated water resources of 56.6 × 100 m^3/year at the surface, and 42.4 × 100 m^3/year underground (PNUD, 1993).

The climate is semi-arid, with strong winds during the dry season, and a mean annual precipitation of 321 mm, mainly due to torrential rains, in the wet season (INGM, 2005). According to the CCKP (2015) in the 1900-2012 years period the mean historical monthly rainfall attained 347.7 mm and the highest value (109.2 mm) was recorded in September. For the same years period the mean historical monthly temperature varied from 20.4 ºC in February to 25.5 ºC in September.

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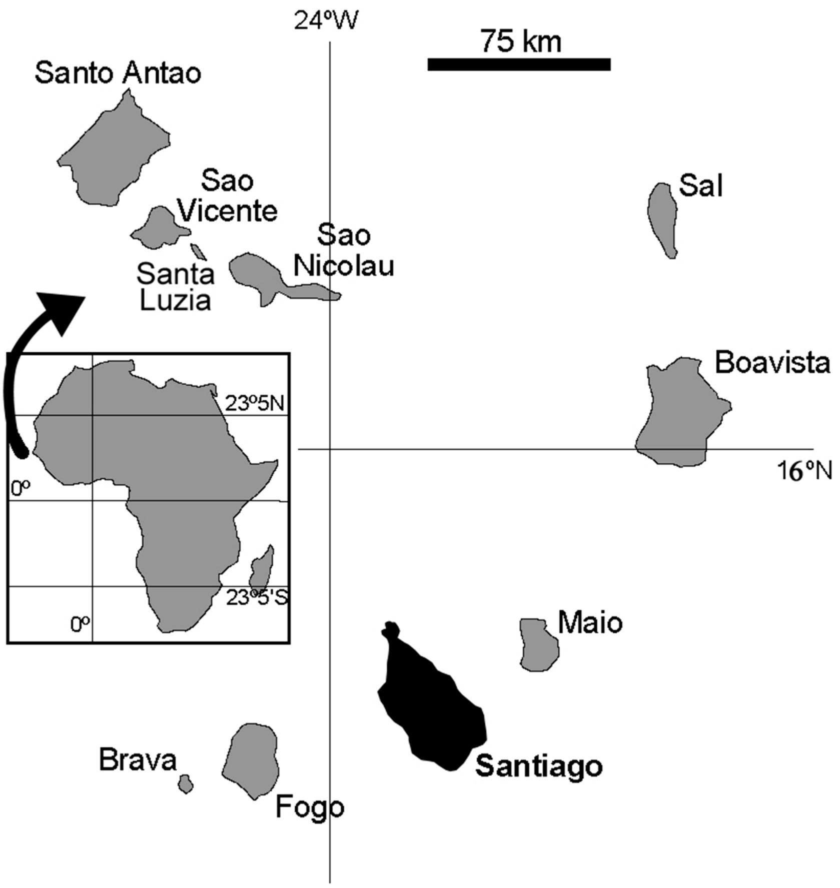

Figure 1 - Cape Verde archipelago and its location.

The islands are volcanic, intraplate, located over a submarine plateau, the Cape Verde Rise, relatively stable within the African Plate and the volcanism resulted from the interaction of a mantle plume with the fractured lithosphere (Williams et al., 1990; Millet et al., 2008). Santiago Island is a shield volcano, with periods of intense volcanic activity, with the emission of alkaline basaltic lava flows and subaerial pyroclastic materials, separated by erosion and sedimentations periods (Serralheiro, 1976). A brief description of the lithostratigraphic formations of Santiago is presented in Figure 2 (a) and Table 1.

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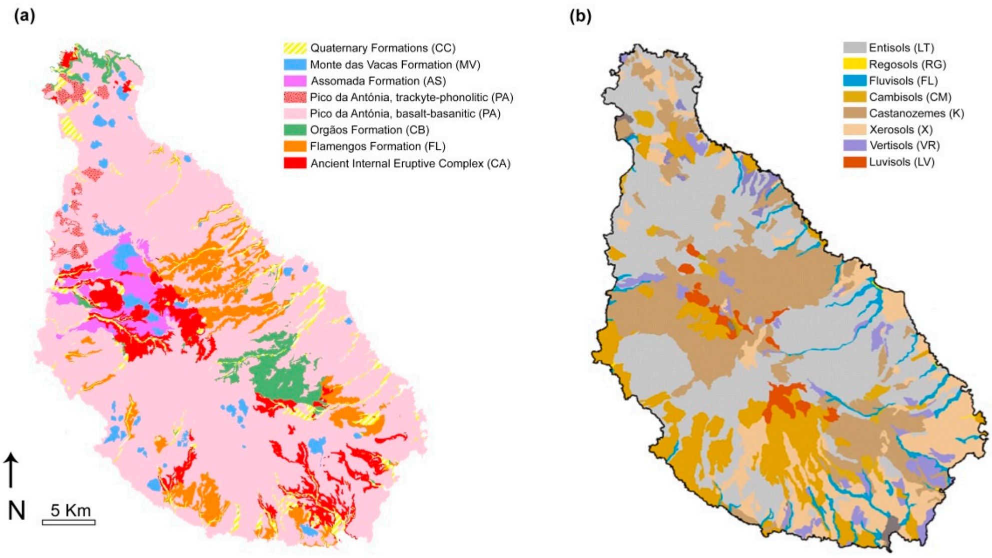

Figure 2(a). Geological cartography of the island of Santiago, Cape Verde, adapted from Serralheiro (1976); **(b).** Adapted soil cartography of the island of Santiago according to FAO/UNESCO Classification (1974), adapted from Hernandez (2008).

Table 1 -Brief description of each geological formation of soils of Santiago Island.

Geological Formation	Rock type	Composition
CA - Ancient Internal Eruptive Complex	Subaerial and submarine lava flows and pyroclastic deposits; dykes and intrusive rocks	Basalts-basanites, phonolites-trachytes and carbonatites
FL – Flamengos formation	Submarine lava flows with subordinated breccias and tuffs	Basanites
CB – Orgãos Formation	Volcano-sedimentary deposits; rare lava flowss	Diverse
PA – Pico da Antónia Eruptive Complex	Subaerial and submarine lava flows, dykes and pyroclastic material; intercalated sedimentary deposits	Basalts-basanites and phonolites-trachytes
AS – Assomada Formation	Subaerial lava flows and some pyroclastes	Basanites
MV- Monte das Vacas Formation	Subaerial pyroclasts and small subordinated lava flows	Basanites
CC – Recent sedimentary formations	Alluvial, aeolian and marine deposits	Diverse

Figure 2 (b) presents the adapted soil cartography of the Santiago Island, based on studies by Faria (1970), Diniz and Matos (1986), Hernandez (2008) and Cabral Pinto et al. (2012), according to the FAO/UNESCO classification and USA Soil Taxonomy. Table 2 shows a brief description of the soil cartography. The main soils are LT, RG, X and CM. Castanozems occur mainly in association with LV, which are the soil group typically used for agriculture in Cape Verde (Figure 2b and Table 2).

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Table 2 -Brief description of each group of soils of Santiago Island.

Pedological Formation	Development characteristics	Texture
LT - Lithosols	Immature incipient mineral soils with no or little differentiation (< 20 cm thickness).	Low clay and organic matter contents and high proportion of coarse-grained fractions.
RG – Regosols	Incipient mineral and undifferentiated soils. No vegetation.	Mainly sandy and gravel materials. Low clay and organic matter contents.
FV – Fluvisols	Undifferentiated or show little differentiation. Developed on alluvial deposits on the banks of temporary or torrential streams.	Mainly sand and coarse particles.
CM – Cambisols	Immature (profile AC), non-climate (20 - 30 cm thickness).	Mainly coarse-to-fine sand with high proportion of slightly weathered rock fragments.
K – Castanozems	Developed soils, but with moderately or poorly differentiated profiles and relatively rich in organic matter.	Fine-grained, mostly consisting of clay materials.
X – Xerosols	Sub-arid soils, with surface decalcification horizons and with some organic matter (0.8–1.8%).	Mainly coarse-to-fine material.
VR - Vertisols	Non-lytic soils. Developed soils (ABC profile).	Fine-grained, up to 30% clay content.
LV – Luvisols	Developed soils (ABC profile).	High proportion of fine-grained particles (mainly clay)

3. Methodologies

3.1. Sampling, chemical and statistical analysis

The sampling, analytical and statistical methodologies were fully described in Cabral Pinto et al. (2015), so only a brief description will be referred in the present paper. Collection of 249 topsoil composite samples, away from potential anthropogenic influence, was performed at a spatial resolution of 0.3 sites/km^2 (identified by GPS). Duplicate field samples were collected at every 10 sites. The <2 mm fraction was pulverized to < 75 µm, digested with *aqua regia* and analyzed by ICP-MS at the ACME Analytical Laboratories, Canada. Lab-duplicate samples were taken at every 30 samples to calculate the analytical precision (which was better than 10%) and certified standard

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materials were analyzed to determine accuracy.

Variance analysis was performed to test the reliability of the data to be used in the statistical analysis. The estimated background values (EBV-S) of the analyzed elements was estimated as the median of the data limited by the Tukey Range. Principal Component analysis (PCA) was performed to determine the associations of metals, with Matlab 10 software.

3.2. Risk assessment

The environmental risk index (ERI) was calculated for PTE by Cabral Pinto et al. (2015) using Canadian (Ministry of the Environment 2011) and Dutch (VROM, 2000), legislations for soils. For each element ERI=C(s)/P, where computed. C(s) is the element concentration at sampling site s and P is the permissive level of that element, according to the legislations.

Non-cancer risk is represented in terms of hazard index (HI) for multiple substances and/or exposure pathways (USEPA, 2011). HI is the sum of the hazard quotient (HQ), for each element and each pathway and if it HI <1 there is a very low chance for a non-carcinogenic risk. HQ = ADD/RfD where ADD is the average daily dose of an element that a person is exposed and RfD is the reference dose (USEPA, 2011), below which the non-cancer risk is negligible.

Hazard indices (HI) were calculated for Co, Cr, Cu, Ni, V, As, Zn, Mn and Cd exposure of Santiago Island population, according to the Exposure Factors Handbook (USEPA, 2011). The equation used to calculate the average daily dose (ADD) for each pathway are those presented in USEPA (2011).

$$\mathrm{ADDingestion} = \frac{\mathrm{Csoil \ x \ IngR \ x \ EF \ x \ ED}}{\mathrm{BW \ x \ AT}} \qquad \text{Eq.- 1}$$

$$\mathrm{ADDdermal} = \frac{\mathrm{Csoil \ x \ SA \ x \ SAF \ x \ DA \ x \ EF \ x \ ED}}{\mathrm{BW \ x \ AT}} \qquad \text{Eq.- 2}$$

$$\mathrm{ADDinhalation} = \frac{\mathrm{Csoil \ x \ InhR \ x \ EF \ x \ ED}}{\mathrm{BW \ x \ AT \ x \ PEF}} \qquad \text{Eq.- 3}$$

Csoil is the concentration of the element in the soil ($mg.kg^{-1}$) and we used the 95 percentile of the soil distribution values, presented in Cabral Pinto et al. (2015). IngR is the soil ingestion rate and we used 200 $mg.d^{-1}$ for children and 100 $mg.d^{-1}$ for adults (USEPA, 2011). EF is the exposure frequency and we used 365 days, considering the

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inhabitants of the island. ED is the exposure duration and we assumed that an inhabitant spend half of is live exposed, so we assumed 6 years for children and 35 years for adults and AT is ED expressed in days for non-carcinogenic. For body weight (BW) we used 15 kg for children and 70 kg for adults and a life expectance of 70 years.

The exposed skin area (SA) was taken as 2372 and 60,132 cm^2 for children and adults, respectively. The used skin adherence factor (SAF) was 0.2 and 0.07 $mg.cm^{-2}$ for children and adults respectively and the dermal absorption factor (DA) was 0.003 for As and 0.001 for other elements (USEPA, 2001; 2011; USDE, 2013). InhR is the inhalation rate taken as 7.6 and 20 $m^3.d^{-1}$ for children and adults, respectively and the particle emission factor (PEF) is $1.36x10^9$ $m^3.kg^{-1}$.

The carcinogenic risks (Risk) were calculated for As, Cd, Cr and Ni exposure of Santiago Island population, according to the Exposure Factors Handbook (USEPA, 2011) and using the RfD values according to USDE (2013).

4. Results and Discussion

The topsoil of Santiago Island is enriched in Cd, Ni, Co, Cu, V, Mn, Cr and Zn to upper crust values (UCC) of Rudnick and Gao (2003), considering both the Estimated Background Values (EBV) or the 95th percentile value calculated from the soil distribution values (Table 3).

Table 3 - Estimated background values, 95 percentiles of Santiago soils ($mg.kg^{-1}$) and ratios of these values to upper continental crust (UCC) and published guidelines values (Gdl).

	EBV	P95(s)	UCC	Guidelines*	EBV/UCC	P95(s)/UCC	EBV/Gdl	P95(s)/Gdl
As	0.6	1.92	4.8	11	0.1	0.4	0.1	0.2
Cd	0.20	0.4	0.09	0.8	**2.22**	**4.4**	**1.1**	0.5
Co	46.4	67.11	17.3	9	**2.7**	**3.9**	**5.2**	**7.5**
Cr	118	298	92	67	**1.3**	**3.2**	**1.8**	**4.4**
Cu	50.8	81.8	28	36	**1.8**	**2.9**	**1.4**	**2.3**
Mn	1293	1954	774.5	-	**1.7**	**2.6**	-	-
Ni	136.1	267.9	47	36	**2.9**	**5.7**	**3.8**	**7.4**
V	169	260	97	86	**1.7**	**2.7**	**2.0**	**3.0**
Zn	79	120.2	67	140	**1.2**	**1.8**	0.6	0.9

EBV: estimated background values[1]; P95(s) 95 percentile in Santiago soils[1]; Gdl: guidelines;
UCC: Upper continental crust[2]; *: Canadian and Dutch Guidelines[3].
[1]Cabral Pinto et al. (2015); [2] Rudnick and Gao (2003); [3] Ministry of the Environment (2011) and (VROM, 2000)

In Santiago Island the soil geochemistry is mainly controlled by lithology, although

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some elements may have an anthropogenic influence, such as As, Hg, Cd, Zn and Pb (Cabral Pinto et al., 2015). Using the permissible values for agricultural soils in the calculations, their results shown that soil of the entire island has environmental risk index (ERI) above 1 for Co, Ni, Cr, V, Cu considering the 95th percentile (Table 3).

The Hazard Quotients (HQ) for ingestion, dermal contact and inhalation routes and Hazard Indices (HI) were calculated (Table 4), for the metals which show enrichment to UCC and also for As, which is a toxic and carcinogenic element, Zn and Mn.

Table 4- HQ values for various pathways and elements and HI for elements from Santiago Island

	HQ ingestion		HQ dermal		HQ inhalation		HI	
	children	adult	children	adult	children	adult	children	adult
Co	2.9827	0.3196	0.0084	0.0013	0.0042	0.0023	2.9952	0.3232
Cr	1.3244	0.1419	0.0037	0.0006	0.0011	0.0006	1.3293	0.1431
V	0.6878	0.0737	0.0019	0.0003	0.0010	0.0005	0.6907	0.0745
Ni	0.1786	0.0191	0.0005	0.0001	0.0011	0.0006	0.1802	0.0198
Cu	0.0273	0.0029	0.0001	0.0000				
As	0.0853	0.0091	0.0007	0.0001	0.0000	0.0000	0.0861	0.0093
Zn	0.0053	0.0006	0.0000	0.0000				
Cd	0.0053	0.0006	0.0006	0.0001	0.0000	0.0000	0.0059	0.0007
Mn	1.1111	0.1190			0.0149	0.0084	1.1260	0.1275

	Cancer risk		
	children	adult	
As	6.4E-09	1.2E-08	for ingestion, dermal contact and inhalation pathways
Cr	3.9E-07	1.3E-06	
Ni	7.2E-09	2.4E-08	for inhalation
Cd	7.8E-11	2.6E-10	

The selected elements are potentially toxic elements and some (As, Cd, Cr and Ni) are also carcinogenic (USDE, 2013). The pathways chosen were ingestion, inhalation and dermal contact and the calculations were performed for children and adults. Major neurodegenerative disorders, including Alzheimer's and Parkinson's disease, are characterized by elevate tissue metals, such as Fe, Cu, Mn and Zn (Barnham and Bush 2008). Environmental exposure to Mn can induce parkinsonism and although the long-term medical significance of this finding is unclear, the data are troubling and point to the need for further investigation of manganese’s health risks (Ahlskog, 2016).

The non-carcinogenic hazard indices (HI) for all nine elements are given in Table 4. For adults the HI are always smaller than 1, whereas for children they are higher than 1 for Co, Cr, and Mn. The HI value of these elements is mainly controlled by the $HQ_{ingestion}$, which are also higher than 1 for these 3 elements. The $HQ_{ingestion}$ is always the highest for all the elements, while the $HQ_{inhalation}$ is the lowest (Figure 3).

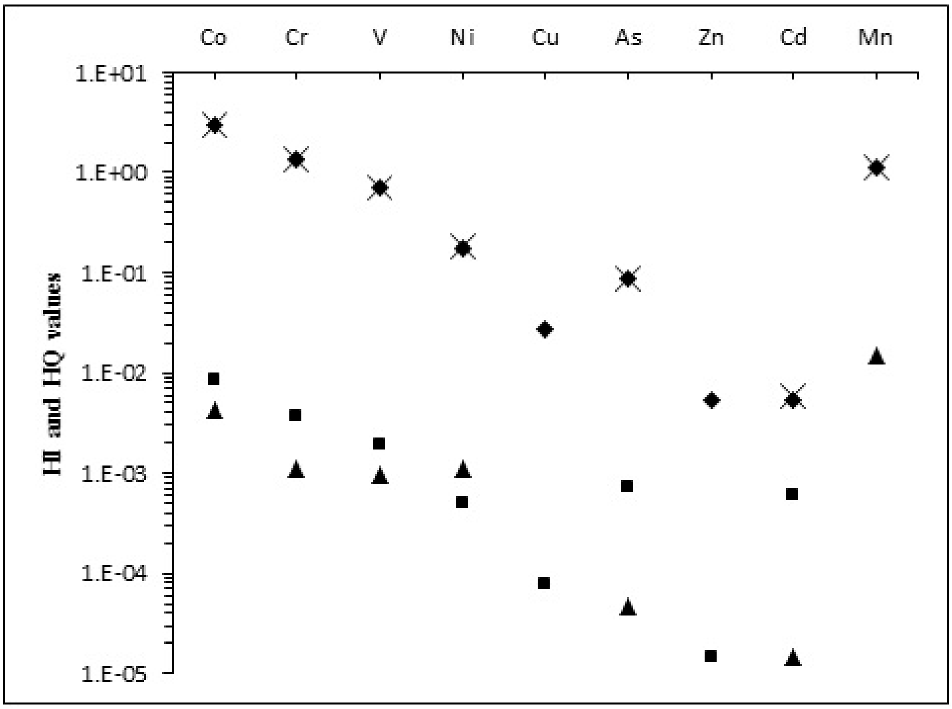

Figure 3- Hazard index (HI) and hazard quotient (HQ) for potentially toxic elements from Santiago Island. Symbols: HI-crosses; HQ for ingestion-diamonds; HQ for dermal contact – squares; HQ for inhalation-triangles.

So there is indication of potential non-carcinogenic risk for children, due to the high Co (HI=2.995), Cr (HI=1.329) and Mn (HI=1.126), values in soils. For the other elements and for adults there is no potential non-carcinogenic risk. For both children and adults the HI is Co>Cr>Mn. Compared to adult, children health index is larger, and their cumulative effect is also of concern for children.

The evaluation of cancer risk was performed only with those elements which are potentially carcinogenic (USDE, 2013). For As, ingestion, inhalation and dermal contact exposure pathways were considered, but for the other carcinogenic elements (Cd, Cr and Ni) only the inhalation risk were computed because the the Risk Assessment Information System (USDE, 2013) does not present slope factors for the other exposures.

For children the As cancer risk ($risk_{total}$) is 6.38 $x10^{-9}$ (Table 4) and of this, the fraction due to $Risk_{ingestion}$ represents 51.6%, while $Risk_{inhalation}$ represents 48.0% and $Risk_{dermalcontact}$ represents only 0.4% of total risk. For adults $risk_{total}$ for As is 1.24 $x10^{-8}$

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(Table 4) where $Risk_{inhalation}$ represents 81.3%, $Risk_{ingestion}$ represents 16.6% and $Risk_{dermal\ contact}$ represents 2.1%. These results reflect the higher daily ingestion dose for children and the higher inhalation rate for adults. For adults the cancer risk due to Cr, Ni and Cd inhalation is always higher than for children, reflecting the higher inhalation rate for adults.

The results for cancer risk are higher than the carcinogenic target risk of $1x10^{-6}$ (USEPA, 2011) only for Cr, for adults, but these results underestimate the risk. The other pathways were not considered and they can be important for Cr, for children which present a cancer risk of $1.3x10^{-6}$, very close to the target risk. The lack of RfD for some elements disenables a more complete evaluation of the cancer-risk.

Santiago Island still has an almost pristine surface environment and the topsoil composition is mainly determined by the composition of the underlying basic rock. These rocks are rich in siderophile elements promoting a natural contamination of soils in Co, Cr, Ni, Cu, V, Zn, Cd and Mn. Of these, Co, Cr and Mn present a potential non-carcinogenic risk for children, which are vulnerable people. On the other way the soil composition affects groundwater composition, so there is a flux of the natural contamination from soils to groundwater which deserves to be evaluated. The inhabitants of Santiago Island depend on groundwater for consumption and for agriculture and the flux water-vegetables-men also deserve evaluation, because endemic diseases can be controlled with proper measures, if its cause is well constrained.

5. Conclusions

The topsoil of Santiago Island, Cabo Verde, have a geochemical composition mainly controlled by the type of underlying rock, as most of the elements in the topsoil have mainly a geogenic origin.

The environmental risk index (ERI) calculations shown that the Santiago Island topsoil are naturally contaminated in Co, Cr, Cu, Ni and V, because these elements have contents well above those allowed by Canadian and Dutch legislations for agricultural soils.

The non-carcinogenic hazard indices (HI) were calculated for 9 potentially toxic elements and they are always smaller than 1 for adults, considering that the soil contaminants enter the human body by soil ingestion, dermal contact and inhalation of

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dust particles. For children the non-carcinogenic hazard indices are 2.9952 for Co, 1.3293 for Cr and 1.1111 for Mn. For the other elements they are lower than 1.

The cancer risk is higher than the carcinogenic target risk of $1x10^{-6}$ for Cr, for adults. But these results may be underestimated as only the inhalation risk was calculated for Cr, Ni and Cd. Also soil contaminants may be indirectly ingested by groundwater and by crop and vegetables consumption. The elements flux soil-groundwater-crops and vegetables may increase the hazard and cancer risk.

There is need of evaluation of the risks associated with groundwater consumption and diet in Santiago Island.

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